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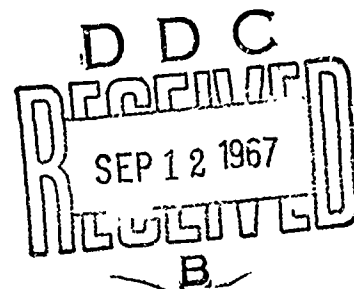
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RESPONSE OF A BURNING PROPELLANT SURFACE TO EROSION TRANSIENTS

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## FOREWORD

The experimental and theoretical studies described in this report are the responsibilities of E. L. Capener and G. A. Marxman, respectively. Major contributors to this research include G. A. Marxman (Principal Investigator), E. L. Capener, C. E. Wooldridge, and R. J. Kier.

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Technical Supervisor for this program is Dr. Bernard T. Wolfson, Project Scientist, Propulsion Division, Directorate of Engineering Sciences, Air Force Office of Scientific Research.

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# ABSTRACT

During the past quarter the analytical model of transient solid propellant combustion has been modified to account for a decrease in gas-phase heat release whenever there is an increase in surface-coupled heat release, and vice versa. The computer analysis has been changed to reflect this modification. Correlation of the numerically predicted behavior with the experimental results obtained previously from traveling wave studies will reveal those factors that are most influential in determining the burning rate response to sudden pressure changes.

Experimental studies of the detailed structure of the flame zone, using fiber optics in conjunction with high-speed photography, have shown that both ammonium perchlorate crystals and aluminum particles may ignite at or near the surface, providing further support for the concept of surface-coupled heat release.

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## NOMENCLATURE

A	frequency factor in Arrhenius law Eq. A2
C	constant defined by Eq. A7
$c_p$	specific heat capacity of gas at constant pressure
$c_s$	specific heat capacity of solid
E	activation energy for pyrolysis at the interface, Eq. A2
$E_D$	activation energy for pressure-insensitive surface-coupled reactions, Eq. A9
$E_f$	activation energy for gas-phase reaction, Eq. A7
$E_H$	activation energy for pressure-sensitive surface-coupled reactions, Eq. A8
h	enthalpy
$h_{g_w}$	energy carried into gas phase with the vaporizing propellant per unit mass
$h_{s_w}$	energy carried by convection from the unreacted solid phase per unit mass
$H_D$	heat release (positive) per unit mass propellant in pressure-insensitive surface-coupled reactions, Eq. A9
$H_H$	heat release (positive) per unit mass propellant (at a reference temperature and pressure) in pressure-sensitive surface-coupled reactions, Eq. A8
K	thermal diffusivity of solid = $k/\rho_s c_s$
k	thermal conductivity of solid
L	heat of vaporization per unit mass of propellant
m	order of heterogeneous reaction Eq. A8; mass flux from the wall
n	order of gas-phase reaction, Eq. A7
p	chamber pressure

$Q_D$	heat of reaction per unit mass of reactant in the pressure-insensitive surface-coupled reaction
$Q_H$	heat of reaction per unit mass of reactant in the pressure-sensitive surface-coupled reaction
$Q_r$	heat of reaction per unit mass of reactant in the gas-phase reaction
$R$	gas constant
$r$	burning rate
$T$	temperature
$t$	time
$x$	distance into the propellant from its surface
$\epsilon_r$	mass fraction of reactant at the propellant surface (nearly unity)
$\rho_s$	density of solid propellant
$\chi$	number of sites which undergo surface-coupled reactions per unit mass of solid propellant

#### Subscripts

$f$	gas-phase flame
$g$	gas phase
$o$	conditions at $x \rightarrow \infty$
$s$	solid phase
$w$	conditions at the wall (gas-solid interface)

## INTRODUCTION

The long-range goal of these theoretical and experimental studies on the combustion instability characteristics of solid propellants is the development of a method for predicting, at an early stage, whether a new propellant will be susceptible to certain types of combustion instability. In the studies performed under the present contract, significant progress has been made in correlating finite-amplitude axial-mode instability with a theoretical analysis of the combustion wave. Furthermore, when laboratory-derived physical-chemical propellant data are substituted into the appropriate expressions, it is possible to compute the critical frequency-response spectrum for a propellant. In addition, when the energy-release distribution within the condensed and gaseous phases is examined, the relative magnitude of the unstable response can be predicted.

Recent studies have been concerned with improving the combustion model, interpreting the fluid dynamic phenomena, and determining experimentally the magnitude of critical ballistic parameters. It has been shown that surface-coupled reactions may be a controlling factor in the incidence of instability. The presence of surface-coupled reactions in ammonium perchlorate propellants was shown early in the program by differential thermal analysis.<sup>1</sup> This phenomenon has since been verified by the fiber-optic studies of the detailed structure of the flame zone that are reported below.

In the continuing development of the analytical model of the combustion wave, the physical assumptions used in developing a mathematically tractable theory have been critically reviewed. It is the objective of the investigation to obtain the information needed to analytically predict the observed instability behavior. Theoretical and experimental developments during the past quarter are described in the present report.

## THEORETICAL STUDIES

In an earlier report on this project<sup>1</sup> the theoretical combustion model developed during the present investigation<sup>2,3</sup> was discussed, with particular emphasis given to features that distinguish this model from others.<sup>4-7</sup> It was shown that the most important of these features is the treatment of surface-coupled reaction kinetics. In terms of the kinetics underlying energetic surface reactions, it has been possible to explain experimentally observed combustion instability behavior with both composite and double-base propellants.<sup>2</sup>

Most of the conclusions drawn from the theory have been based on a linearized analysis;<sup>2</sup> the chief advantage of such an analysis is the physical clarity with which the implications of the model are revealed. However, to obtain a quantitative comparison with finite-amplitude combustion oscillations, such as those observed in the present axial-mode instability studies, it is necessary to account for nonlinear effects in the analysis. For this purpose, a computer program based on the nonlinear equations of the model is being developed. This computer program incorporates a slightly modified version of the combustion model that evolved from theoretical studies during the past quarter of this investigation. This modification becomes significant only when large-amplitude oscillations (i.e., nonlinear phenomena) are under consideration.

A brief review of the combustion model presented earlier,<sup>2,3</sup> and a discussion of some of its main features, appears in the Appendix of this report. This Appendix provides useful background for the following discussion of the recent theoretical work leading to the modified model.

### Predicted Steady-State Behavior of the Flame Temperature

Unlike many other combustion models, the model summarized in the Appendix predicts that the gas-phase flame temperature will increase as the burning rate rises, even in steady-state combustion. This behavior is a consequence of the surface-coupled reaction kinetics



employed in the model, as will become evident from a careful examination of Eq. 1. (This equation, which is a boundary condition, is derived in the appendix and appears there as Eq. A10.)

$$-k\left(\frac{\partial T}{\partial x}\right)_w = \rho_s r \left[ \epsilon_r Q_r - L - c_p(T_f - T_o) + c_s(T_w - T_o) + H_H\left(\frac{p}{T_w}\right)^m e^{-E_H/RT_w} + H_D e^{-E_D/RT_w} \right] \quad (1)$$

In steady-state combustion, the net heat flux into the unreacted solid propellant is equal to the energy required to condition the propellant for surface pyrolysis, i.e.,  $-k(\partial T/\partial x)_w = \rho_s r c_s(T_w - T_o)$ . Thus, in the steady-state limit, Eq. 1 becomes a simple expression for the gas-phase flame temperature in terms of the total heat release in the combustion process:

$$c_p(T_f - T_o) = \rho_s r \left[ \epsilon_r Q_r + H_H\left(\frac{p}{T_w}\right)^m e^{-E_H/RT_w} + H_D e^{-E_D/RT_w} - L \right] \quad (2)$$

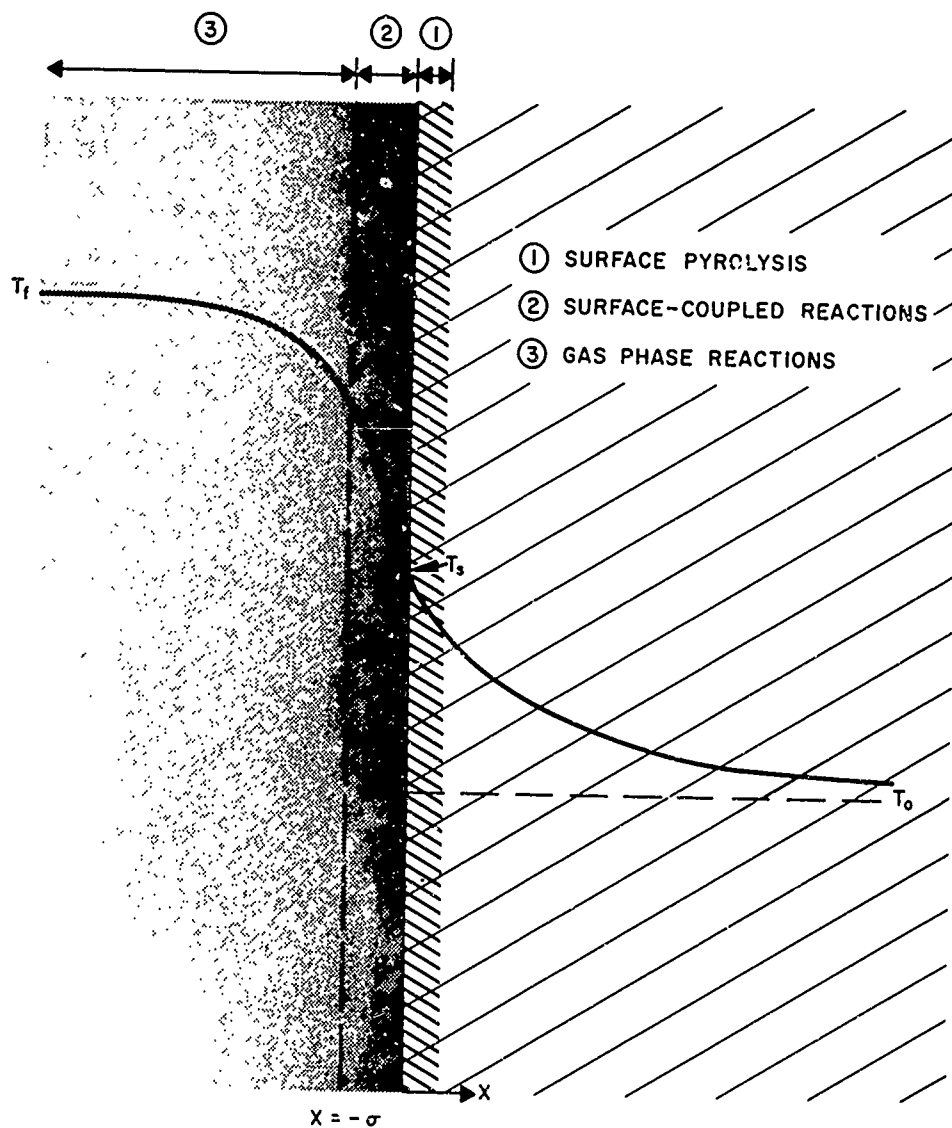
The first term within the brackets of this equation represents the heat release associated with combustion in the gas-phase flame; the next two terms describe, respectively, pressure sensitive (heterogeneous) and pressure insensitive energetic surface-coupled reactions; the last term represents the latent heat of phase change or decomposition near the burning surface. As the burning rate increases, so does  $T_w$  (see Eq. A2 of the Appendix). Thus, the magnitude of the surface-coupled heat release increases with burning rate, and it follows from Eq. 2 that  $T_f$  rises as well. For a reasonable choice of parameters such as  $E_H$  and  $E_D$ , a large change in pressure (and therefore burning rate) may lead to a greater increase in  $T_f$  than is normally encountered with actual propellants. (Composite propellants typically exhibit a modest increase in flame temperature with pressure up to about 200 psi, after which  $T_f$  is almost constant. Double-base propellants often have a somewhat greater dependence of flame temperature on pressure in steady-state combustion.)

The characteristic just described suggests that a modification of the model may be in order, because the accuracy with which the model predicts the steady-state behavior of all dependent variables may be regarded as a legitimate test of its applicability to nonsteady phenomena. In general, the model in its present form, as summarized in the Appendix, will not yield the exact steady-state behavior of flame temperature versus pressure for a given propellant unless certain restrictions are imposed on the numerical values assigned to kinetics parameters such as  $E_H$  and  $E_D$ . This situation is not entirely satisfactory, because the flame temperature is actually a purely thermodynamic quantity, determined primarily by the heat of reaction of the propellant; it is quite independent of the reaction kinetics. (Note that  $T_f$  is normally obtained from an "adiabatic flame temperature" calculation, in which the propellant composition and heats of reaction appear but not the kinetics parameters.<sup>8</sup>

To identify the source of this apparent anomaly in the combustion model, it will be helpful to re-examine the theoretical description of gas-phase and surface-coupled heat release in the combustion process. A brief study of the steady-state combustion mechanism will reveal a minor but potentially important correction that should be introduced into the model to overcome the difficulty described above, and it will also clarify the physical basis for the surface kinetics treatment that earlier<sup>2,3,9</sup> was shown to be the most important feature of the model.

#### Theoretical Description of the Distribution of Heat Release in Solid Propellant Combustion

The solid propellant combustion mechanism is illustrated in Fig. 1. It is convenient to envision the propellant as moving at a negative velocity, equal to the burning rate, toward the surface zone ( $x = 0$ ) where pyrolysis occurs; the pyrolysis products then proceed into the gas phase where further reactions complete the combustion and the final flame temperature  $T_f$  is achieved. During this process the total



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FIG. 1 SIMPLIFIED MODEL OF THE DISTRIBUTION OF HEAT RELEASE IN THE SOLID PROPELLANT COMBUSTION PROCESS

heat release per unit area of propellant surface, and per time, is  $\rho_s r Q$ , where  $Q$  is the total heat of combustion of the propellant. Of this total, a portion,  $\rho_s r Q_s$ , is released within a relatively narrow pyrolysis region near the surface of the solid; i.e.,  $Q_s$  is the heat of decomposition of the propellant. In a typical ammonium perchlorate type composite propellant, for example,  $Q_s$  would be essentially the heat of decomposition of ammonium perchlorate. The pyrolysis products then initiate a very complex sequence of reactions, which occurs in a zone extending from the propellant surface into the gas phase for whatever distance is required to complete combustion. The thickness of the gas-phase flame zone depends on both the total mass flux  $\rho_s r$  and the kinetics of the reactions within this zone. For example, as the pressure increases the local reactant concentration rises, causing an increase in the local reaction rates. Thus, at higher pressures the reactions are accomplished more rapidly and the flame zone is thinner, as is well known.

To express the total heat release in the combustion process in terms of that associated with each of the constituent reactions, it is convenient to define a parameter  $\epsilon$ , which is essentially a measure of the "completeness" of combustion. Specifically, the concentration of reactants entering any given reaction plane in the flame zone, such as  $x = -x_1$ , is  $\rho_s r [1 - \epsilon(x_1)]$ . At the gas-solid interface  $\epsilon \ll 1$ , because the flow at that point consists almost entirely of pyrolysis products that are available for further reactions. As the distance from the propellant surface grows larger,  $\epsilon$  increases, since more and more combustion products are present and the concentration of potential reactants is less. The position at which  $\epsilon = 1$  marks the edge of the flame zone; i.e., when  $\epsilon = 1$  there are no more reactants, combustion is complete, and the flame temperature has been achieved.

This visualization of the combustion process leads to the following relatively simple expression for the total heat release per unit time and surface area:

$$\rho_s r Q = \rho_s r Q_s + \rho_s r \int_0^{-\infty} H(x) [1 - \epsilon(x)] e^{-E(x)/RT(x)} dx \quad (3)$$

As was noted above, the concentration factor  $\epsilon$  is a function of  $x$ , changing from nearly zero at the propellant surface to unity at the edge of the flame zone. In addition, the local heat of reaction  $H$ , the local activation energy  $E$ , and the temperature  $T$  vary with  $x$ . All of these variables depend on the specific sequence of reactions involved in the process; at any given position  $x_1$ , the quantities  $H$  and  $E$  characterize the particular reaction occurring at that point, whereas  $\epsilon$  and  $T$  reflect the history of reactions closer to the surface. To perform the integration of Eq. 3 it would be necessary to assume a specific reaction sequence and solve the conservation equations to determine the concentration and temperature profiles. This would be a formidable task, hardly justifiable or even possible in view of our generally poor knowledge of details of the reactions in the flame zone. Nevertheless, Eq. 3 suggests some interesting and useful concepts for the combustion model.

First, note that Eq. 3 expresses the total heat release in terms of the constituent reactions in either steady or nonsteady combustion. Second, note that as the general temperature level rises, as when the burning rate or pressure increases, the integral is completed over a shorter distance, i.e., the flame zone is thinner. Alternatively, as the temperature increases, a greater fraction of the total heat release occurs within an arbitrarily narrow zone of thickness  $\sigma$  (Fig. 1) near the surface. This observation is important in nonsteady combustion, because those reactions near the surface will be "surface-coupled," or governed primarily by the relatively slow thermal response of the solid, whereas those farther out in the flame zone will follow the much faster thermal response of the gas. It is this aspect that led to the unique kinetics description of surface-coupled reactions employed in the SRI theory,<sup>3,9</sup> as will be demonstrated presently.

#### Modification of the Combustion Model

In principle the combustion model described in the Appendix should contain the right-hand side of Eq. 3 in place of the first and the last two terms of Eq. A10, which represent the gas-phase and the

surface-coupled heat release, respectively. However, in this form the combustion model would almost exclude the possibility of reasonable mathematical analysis, as was explained in connection with Eq. 3. Therefore, it is necessary to introduce a major simplification while retaining those features of Eq. 3 that are of major importance in both steady and nonsteady combustion. This simplification is accomplished by dividing the flame zone into two regions: one relatively thin zone adjacent to the propellant surface (e.g., the zone of thickness  $\sigma$  in Fig. 1) and the other occupying the remainder of the flame zone. Reactions in the first zone occur practically at the surface temperature  $T_w$ , and in nonsteady combustion the temperature profile in this region tends to be in phase with  $T_w$ ; i.e., it is dominated by the thermal response of the solid phase. This is the zone of surface-coupled reactions and it is characterized by the fact that  $\epsilon \ll 1$ . The other zone encompasses the "true" gas-phase reactions, or those that follow the faster thermal response of the gas phase. With this approach Eq. 3 takes the following much simpler form:

$$\rho_s r Q = \rho_s r \left\{ Q_s + \int_{x=-\sigma}^{-\infty} H(x) [1 - \epsilon(x)] e^{-E(x)/RT(x)} dx \right\} + \rho_s r H e^{-E/RT_w} \quad (4)$$

A comparison of Eq. 4 with Eq. 1 shows that the last term of Eq. 4 represents the surface-coupled heat release; this term has been separated into two parts in the combustion model: one describing pressure-sensitive or heterogeneous reactions, and the other those that are pressure insensitive. The bracketed quantity in Eq. 3 is clearly identified with  $Q_r$  in Eq. 1.

This comparison reveals at once the modification that should be introduced into the model for application to nonlinear behavior. In the model,  $Q_r$  has heretofore been treated as a constant, whereas Eq. 4 shows that it may vary. The way it varies for a given propellant is determined by the behavior of the total heat of reaction,  $Q$ , which can be determined from thermochemical calculations. (In fact, knowing the

dependence of  $Q$  on pressure in steady combustion is equivalent to knowing the behavior of the flame temperature,  $T_f$ .) If  $Q$  is known, then for any value of the last term in Eq. 4,  $Q_r$ , which corresponds to the quantity in brackets, is also known. Thus, for large excursions in the pressure or burning rate,  $Q_r$  should be treated as a variable such that in the steady-state limit the dependence of the flame temperature on the pressure is as predicted by thermochemical calculations. Note that this method of ensuring a correct flame temperature behavior in the model involves only the heats of reaction and is completely independent of the kinetics parameters, such as  $E_H$  and  $E_D$ . In this way the objection raised earlier in this report, relevant to the original form of the model, is completely overcome.

It can be shown that the influence of a varying  $Q_r$ , relative to a constant  $Q_r$  in Eq. 1, is a second-order effect. Therefore, it was possible to use the assumption  $Q_r = \text{constant}$ , as in the Appendix, for previous linearized analyses,<sup>3,9</sup> which simplifies the treatment somewhat. However, for a nonlinear analysis, such as the computer program described in the following section, the modified combustion model with variable  $Q_r$  is needed. Inasmuch as the foregoing discussion has centered on steady-state combustion, a brief commentary on the method of modifying the model for a nonsteady analysis is in order.

In general, the behavior exhibited by Eq. 4, or by Eq. 1 with a variable  $Q_r$ , is as follows: As the burning rate and surface temperature rise, the amount of surface-coupled heat release increases. Normally, the total heat release increases too, but only slightly. Therefore,  $Q_r$  must decrease as the surface terms increase to preserve the correct total heat release,  $Q$ . The dependence of the surface terms on  $T_w$  or on the burning rate (see Eq. A2) is known. The dependence of the adiabatic flame temperature, and therefore of  $Q$ , on the pressure (or the burning rate or  $T_w$ ) is known from thermochemical calculations. The difference between  $Q$  and the surface terms is  $Q_r$ , and the thermochemical calculation establishes a unique value of  $Q_r$  for every value of  $T_w$  and the surface terms.

It appears reasonable to assume that in nonsteady combustion the heat release in the gas phase,  $Q_r$ , will be the same as the steady-state value for the same total heat release in the surface-coupled terms. Note that this assumption does not relate  $Q_r$  to the instantaneous value of  $T_w$  or  $p$ , but to the instantaneous heat release, thereby preserving the thermochemical characteristics of the propellant. In the steady-state limit this assumption reduces to the correct behavior, as described above.

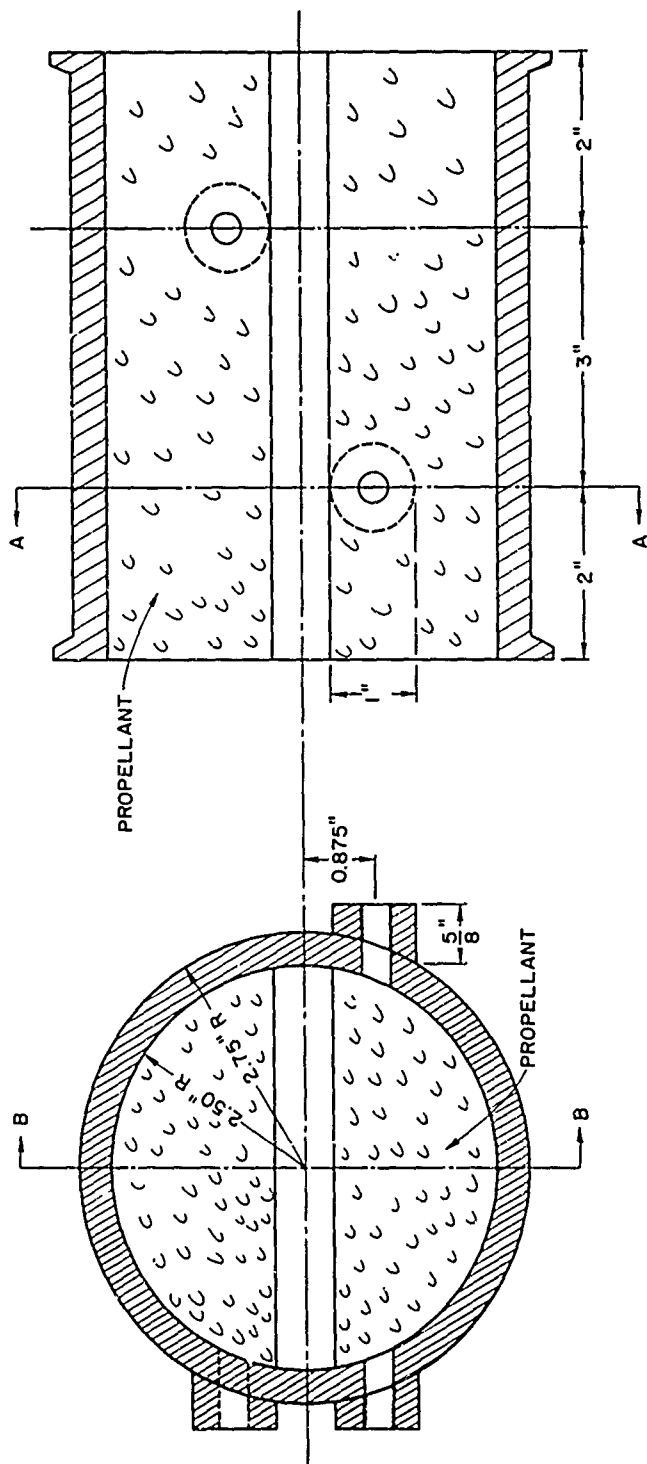
For the computer program described below, the combustion model has been modified according to the method just described.



## EXPERIMENTAL STUDIES

The preliminary experiments using fiber optics to study the flame zone of burning solid propellants have provided insight into the micro-structure of the flame zone. Magnification in this region is sufficient to reveal details from the surface out to about 2000 microns. The slab burner used for this study is shown in Fig. 2. The upper half of the burner contains a single viewing port for use when self-illumination from the flame zone is being photographed. The lower half of the burner contains two opposed viewing ports which are used when back-lighting is required; e.g., for schlieren or shadow photography. The combustor is 2 inches I.D. by 6 inches long and is terminated by the sample holder at one end and a copper nozzle at the other end. Pyrex fiber optics which are 1/8 inch diameter are screwed into the viewing ports; a high-speed camera, which can operate at framing rates up to about 9000 per second, is used to view the burning surface as it recedes past the fiber optic.

The initial photographs without back lighting revealed that the combustion zone is frequently disturbed by the explosive deflagration of single ammonium perchlorate (AP) crystals. Photographs of the deflagrating crystals in a propellant containing 80% ammonium perchlorate (AP) and 20% polyurethane (PU) were presented in the last report.<sup>1</sup> Figure 3 is a more recent shadowgraph obtained at a chamber pressure of 185 psia with backlighting provided by a mercury arc lamp. The sequence of pictures shown is taken from a movie film which was shot at 8500 frames per second; the first four frames shown represent events 0.235 msec apart in time, and the last frame follows the fourth by 0.118 msec. Frame (a) shows the emergence of an AP crystal above the burning surface. In frame (b) ignition is clearly seen to occur on two faces of the crystal; combustion then continues until ultimately, in frame (e), a final burning bit is seen to leave the surface. This particular crystal is somewhat atypical, in the sense that its diameter is about 400 microns, but smaller crystals which are more difficult to observe should behave in a similar manner.

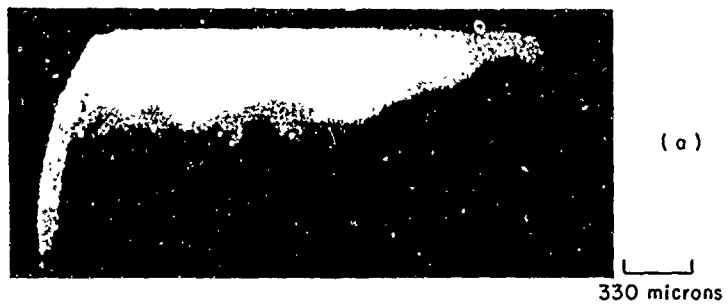


SECTION A

SECTION B

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FIG. 2 TEST MOTOR USED TO OBTAIN FIBER OPTIC PHOTOGRAPHS



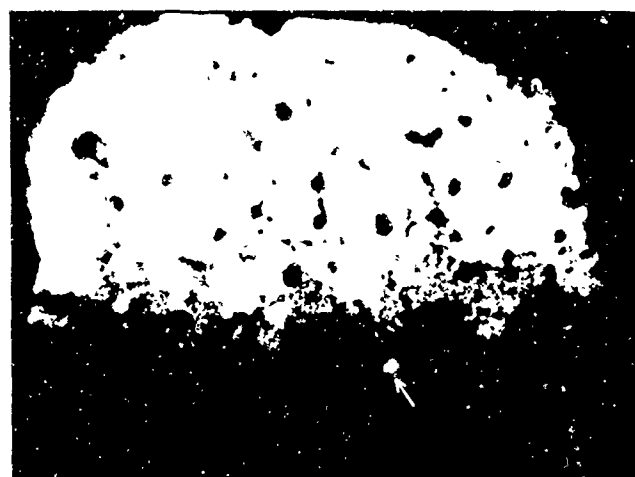
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FIG. 3 FIBER OPTIC SHADOWGRAPH SHOWING THE DEFLAGRATION OF AMMONIUM PERCHLORATE AT THE SURFACE OF A BURNING SOLID PROPELLANT

Figures 4 and 5 show the ignition and subsequent partial combustion of aluminum particles at the burning surface. This particular propellant contained 5 percent aluminum by mass. The framing rate was 8500 per second, giving 0.118 msec between frames; these pictures were obtained without backlighting. Frame (a) of both figures shows a glowing aluminum particle, about 50 microns in diameter, in place on the propellant surface. Ignition occurs in frame (b), and in frame (c) the burning particle is seen to leave the surface.

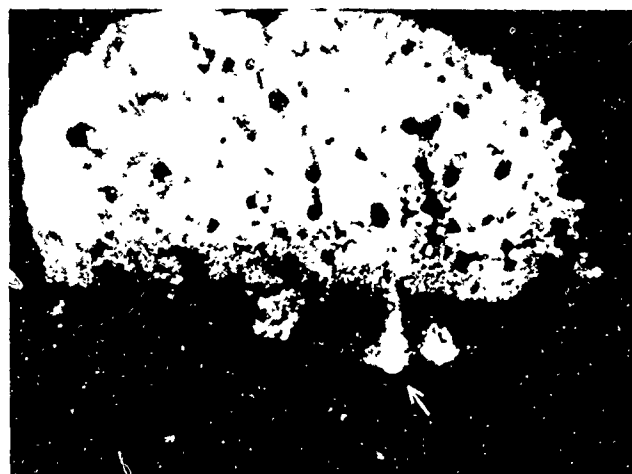
These two sequences are representative of many that are observed during a typical test. The fact that aluminum ignition occurs at the surface is noteworthy because the temperature of approximately  $1000^{\circ}\text{K}$  in this region is far below the  $2300^{\circ}\text{K}$  ignition point of aluminum in oxygen. This implies that ignition must be induced by intermediate products of the perchlorate decomposition process.

In summary, Figs. 3, 4, and 5 definitely indicate that important heat release phenomena do occur in the vicinity of the surface, lending experimental support to the analytical model.

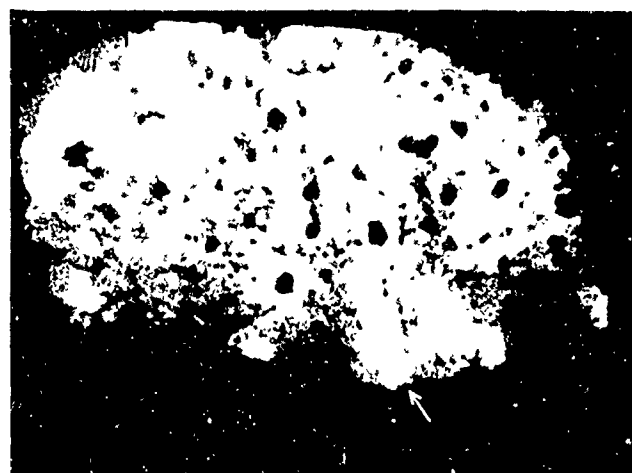


(a)

330 microns



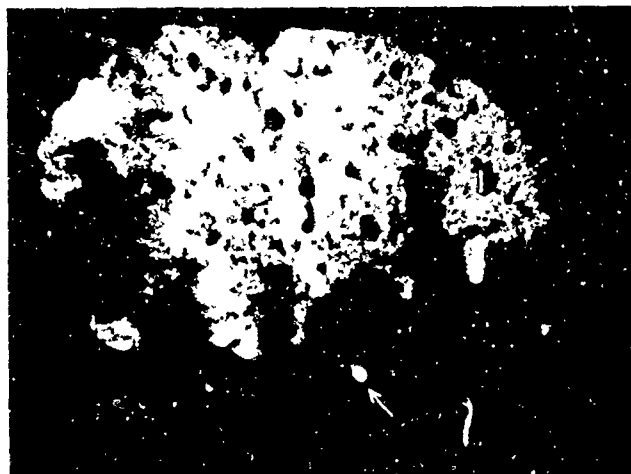
(b)



(c)

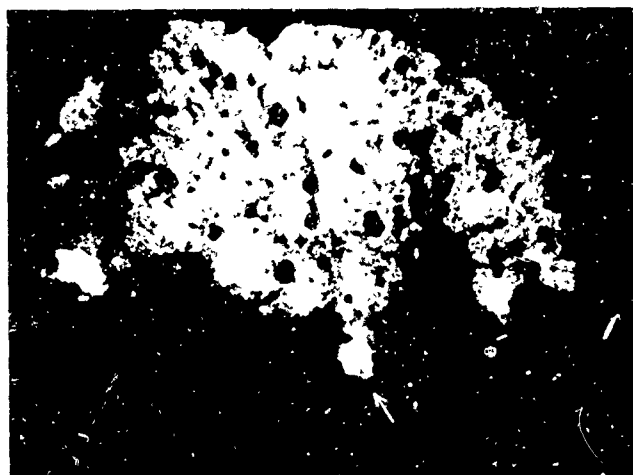
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FIG. 4 FIBER OPTIC VIEW OF THE IGNITION OF ALUMINUM PARTICLES  
AT THE SURFACE OF A BURNING SOLID PROPELLANT



(a)

330 microns



(b)



(c)

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FIG. 5 FIBER OPTIC VIEW OF THE IGNITION OF ALUMINUM PARTICLES  
AT THE SURFACE OF A BURNING SOLID PROPELLANT

## FUTURE STUDIES

As has been noted, a nonlinear analysis of the combustion model is in preparation. This analysis will be obtained by programming Eqs. A1, A2, A3, A7, and A10 for a digital computer, with Eq. A10 modified according to the method described in the present report. The computer program is nearly completed and will be used during the coming quarter for comparisons with earlier results.

Additional theoretical studies have been initiated to clarify the gas-dynamical mechanism by which the combustion mechanism, responding to pressure pulses induced by traveling shock waves in the chamber, interacts with the shock waves to create combustion instability. Earlier studies under this contract have clearly established the relationship between propellant response and the existence of combustion instability. The remaining unknown in the process is the precise mechanism through which an oscillatory burning rate, when it exceeds a certain amplitude, can prevent the decay of a traveling shock wave in the motor and thereby sustain combustion instability. If this mechanism can be determined, the theoretical explanation of axial-mode, traveling-wave combustion instability observations will be complete.

The chief objective of the experimental studies during the remainder of the program will be to provide insight and guidance for the theoretical studies mentioned above. For this purpose the fiber-optic technique described in the present report appears promising. Therefore, our future experimental effort will focus on further development of the fiber-optic method; the ultimate goal will be direct observation of the combustion process as shock waves pass over the surface. Such observations should contribute significantly to our understanding of the interaction between the combustion response and the traveling waves in the chamber.

## APPENDIX

### THEORETICAL COMBUSTION MODEL FOR TRANSIENT BURNING OF A SOLID PROPELLANT

#### Formulation of the Combustion Model

To clarify the differences between the various combustion models, it will be convenient to repeat here the mathematical formulation of the SRI combustion model, as it was presented earlier.<sup>3,9</sup>

The chief assumptions made in the analysis are the following:

(a) the gas-phase reactions can be represented in terms of a single reaction of arbitrary order that obeys Arrhenius kinetics and responds instantaneously to pressure and temperature disturbances (i.e., time-dependent terms are omitted in the gas-phase equations); (b) the Lewis number is unity in the gas phase; (c) surface pyrolysis and surface-coupled exothermic or endothermic reactions follow Arrhenius laws; and (d) the solid phase is essentially homogeneous with temperature-independent transport properties. For typical propellants, assumption (a) is valid for chamber oscillations at frequencies of a few thousand cps or less. Most of the acoustic instability problems of greatest interest fall within this regime.

As (b) implies, the pyrolysis and surface-coupled reactions are assumed to occur in a surface layer of negligible thickness relative to the penetration depth of the temperature profile. It is difficult to evaluate the quantitative effect of assumptions (b), (c), and (d). However, it is important to remember that all analyses of this kind unavoidably rely on a highly simplified picture of the complex combustion process. Within this context these assumptions are fully justified, even necessary, because they permit a simplified mathematical formulation that is consistent with the underlying concepts.



The formulation begins with the equation governing heat conduction in the solid phase beyond the surface reaction zone:

$$\frac{\partial T}{\partial t} = r(t) \frac{\partial T}{\partial x} + K \frac{\partial^2 T}{\partial x^2} \quad (A1)$$

The propellant pyrolysis at the wall is assumed to follow an Arrhenius law so that the burning rate is related to wall temperature as follows:

$$r = a e^{-E/RT_w} \quad (A2)$$

The following boundary condition is imposed upon the temperature:

$$x \rightarrow \infty; \quad T \rightarrow T_o \quad (A3)$$

The remaining boundary condition is obtained through an energy-flux balance at the gas-solid interface. The net heat conducted into the unreacted solid propellant from the interface at the plane  $x = 0$  is

$$-k \left( \frac{\partial T}{\partial x} \right)_w = -k \left( \frac{\partial T}{\partial x} \right)_{g_w} - \rho_s r h_{g_w} + \rho_s r h_{s_w} + Q_H + Q_D \quad (A4)$$

The first term on the right-hand side of the equality sign represents the energy coming from the gas phase; the second, the energy carried into the gas with the vaporizing propellant; the third, the energy carried by convection from the unreacted solid phase into the interface; the fourth, the energy released (positive) in heterogeneous decomposition reactions at the surface whose reaction rates depend upon the local gas-phase density; and the last, the energy released in solid-phase surface reactions with rates that are independent of gas-phase conditions. It is convenient to rewrite this expression as follows:<sup>10</sup>

$$-k \left( \frac{\partial T}{\partial x} \right)_w = -k \left( \frac{\partial T}{\partial x} \right)_{g_w} + \rho_s r [(c_s - c_p)(T_w - T_o) - L] + Q_H + Q_D \quad (A5)$$

Denison and  $\pi^{10}$  have obtained a solution to the gas-phase conservation equations by assuming that the complex gaseous reaction process can be represented by a single-step reaction of order  $n$ , where in some cases  $n$  may not be an integer. We have retained their gas-phase solution, which yields the following expression for the heat flux from the gas phase to the wall:

$$-k \left( \frac{\partial T}{\partial x} \right)_{g_w} = \rho_s r [\epsilon_{r_w} Q_r - c_p (T_f - T_w)] \quad (A6)$$

This solution also relates the instantaneous flow of reactant into the gaseous reaction zone,  $\rho_s r$ , to the instantaneous gas-phase reaction rate so that

$$r = C_p^{n/2} T_f^{(n/2)+1} e^{-E_f/2RT_f} \quad (A7)$$

The above derivation assumes that the surface-coupled reactions occur in a thin zone so that the surface heat release acts as a boundary condition on the solid phase. To derive a suitable kinetics description, the solid propellant can be thought of as containing possible reaction sites such that

$$\rho_s r \chi = \begin{array}{l} \text{number of sites which} \\ \text{undergo reaction per} \\ \text{unit area of reaction} \\ \text{zone per unit time} \end{array}$$

where  $\chi$  is the number of sites that undergo reaction per unit mass of material. The heterogeneous heat release can now be expressed in terms of the above expression and an Arrhenius law as

$$Q_H = \rho_s r H_H \left( \frac{p}{T_w} \right)^m e^{-E_H/RT_w} \quad (A8)$$

for a pressure-sensitive reaction. The parameter  $\chi$  has been absorbed in  $H_H$ , the heat release per unit mass. Note that  $H_H$  may depend upon the thickness of the surface reaction zone (which is related to  $\rho_s r$ ) and upon the specific character of the pyrolysis process (which is also related ultimately to  $\rho_s r$ ). For example, one might choose to write the above kinetics expression with  $(\rho_s r)^y$ , instead of  $\rho_s r$ . Then the exponent  $y$  would become an unknown, and somewhat indirect, measure of the extent of surface reactions relative to gas-phase reactions. However, such a modification does not significantly alter the conclusions drawn from the analysis. Therefore, until there emerges a more detailed understanding of the mechanism, any further complications of this type probably are unwarranted and have not been considered.

Except that they are independent of the pressure, the other surface reactions follow a similar law:

$$Q_D = \rho_s r H_D e^{-E_D/RT_w} \quad (A9)$$

Equations A5, A6, A8, and A9 can be combined to obtain:

$$\begin{aligned} -k \left( \frac{\partial T}{\partial x} \right)_w = & \rho_s r \left[ \epsilon_{r_w} Q_r - L - c_p (T_f - T_o) + c_s (T_w - T_o) \right. \\ & \left. + H_H \left( \frac{p}{T_w} \right)^m e^{-E_H/RT_w} + H_D e^{-E_D/RT_w} \right] \quad (A10) \end{aligned}$$

Equations A1, A2, and A7, with the boundary conditions of Eqs. A3 and A10, complete the mathematical representation of the combustion model in terms of the dependent variables  $T_f$ ,  $T_w$ , and  $r$ . Owing to the non-linear character of these equations, a closed-form solution cannot be obtained, in general. A linearized solution has been presented in detail previously.<sup>3,4,9</sup>

### Comparison of the SRI Theory with Other Response Function Theories

As has been mentioned, the most significant difference between the formulation above and other combustion models lies in the method of accounting for surface reactions. It has been the usual practice in virtually all other theories to employ what may be described as a "one-step" description of surface kinetics. Specifically, the quantities  $Q_H$  and  $Q_D$  (Eqs. A4 and A5) have been assumed to be proportional to the burning rate  $r$  alone. If one follows this procedure, the Arrhenius temperature dependence of the last two terms in Eq. A10 vanishes. This general approach has been used at SRI to describe double-base propellants only, by letting  $E_H = E_D = 0$  in Eq. A10. Such a treatment leads to results in good agreement with double-base experiments.<sup>2</sup> However, it is felt that the more complex "two-step" description of Eq. A10 is necessary for composite propellants, and the experimental results tend to confirm this assumption. A physical interpretation of the surface reaction process that we are trying to describe in composite and double-base propellants, respectively, will clarify the reasoning that led to the kinetics description incorporated in Eq. A10.

For composite propellants we may envision the surface reaction zone as encompassing, first, pyrolysis of the propellant (described by Eq. A2 and subsequently, surface-coupled reactions among the pyrolysis products (described by Eqs. A8 and A9). Thus, the activation energies  $E_H$  and  $E_D$  associated with Eqs. A8 and A9 represent an overall description of a complicated sequence of events, which may include mixing between the various macroscopic constituents of the composite propellant, as well as reaction steps. In contrast, with a double-base propellant there is no reason to distinguish surface-coupled energetic reactions from pyrolysis reactions, because the constituents are intermixed on a molecular scale. Thus, the pyrolysis and other reactions may be considered as a single sequence, with a single activation energy,  $E$ , characterizing the rate-controlling step, and with  $E_H = E_D = 0$ . A possible exception might occur with heterogeneous reactions, which could call for a very small value of  $E_H$  associated with molecular mixing between gas-phase constituents and pyrolysis products.

In summary, according to this interpretation a composite propellant generally corresponds to  $E_H > 0$  and/or  $E_D > 0$ , whereas for a typical double-base propellant  $E_H = E_D = 0$ . It follows from the SRI theory<sup>2,3</sup> that exothermic surface-coupled reactions tend to destabilize composite propellants (by increasing the response amplitude), while they tend to stabilize double-base propellants. This rather remarkable theoretical conclusion may explain the previous experimental observation that the stable-burning regimes of composite and double-base propellants are reversed.<sup>11</sup> It is important to recognize that the possibility of a destabilizing effect associated with surface-coupled exotherms does not arise unless there is a departure from the single-step description of the surface kinetics (i.e.,  $E_H = E_D = 0$ ). Because earlier treatments have employed only the single-step description, they have not predicted this effect.

It is evident from the foregoing discussion that the method of incorporating surface reactions in the combustion model is a crucial factor. All the experimental results obtained in our laboratory<sup>2,11</sup> associate surface exotherms with instability in composite propellants. Earlier analyses based on simpler kinetics descriptions predict the opposite behavior, whereas the present treatment is consistent with the observations. Additional support comes from the following considerations: (1) The resonance amplitudes and frequencies indicated by the theory are in agreement with experimental observations<sup>12</sup> of typical propellants, within the accuracy of experiment or theory; (2) observed shifts in the resonance curves and other striking consequences of composition alterations are also anticipated within the context of the theory; and (3) the analysis suggests a plausible explanation for the rather striking differences in the behavior of composite and double-base propellants. These factors strongly suggest that an approach similar to that employed in the present investigation is necessary for an acceptable representation of the combustion mechanism.

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13. ABSTRACT <p>This report covers the research progress on combustion instability characteristics of solid propellants accomplished under Contract AF 49(638)-1665, during the period 1 April through 30 June 1967.</p> <p>During this quarter the analytical model of transient solid propellant combustion has been modified to account for a decrease in gas-phase heat release whenever there is an increase in surface-coupled heat release, and vice versa. The computer analysis has been changed to reflect this modification. Correlation of the numerically predicted behavior with the experimental results obtained previously from traveling wave studies will allow the determination of those factors that are most influential in determining the burning rate response to sudden pressure changes.</p> <p>Experimental studies of the detailed structure of the flame zone, using fiber optics in conjunction with high-speed photography, have shown that both ammonium perchlorate crystals and aluminum particles may ignite at or near the surface, providing further support for the concept of surface-coupled heat release.</p>			



